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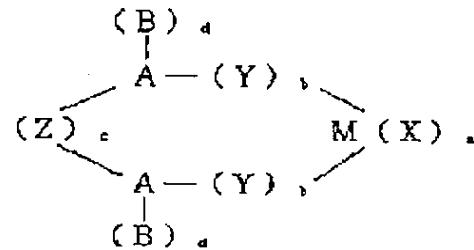
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(54) CATALYST FOR POLYMERIZATION OF OLEFIN AND PRODUCTION OF POLYOLEFIN USING THE CATALYST

(57) Abstract:

PURPOSE: To provide an olefin polymerization catalyst comprising a specific transition metal compound, a compound capable of forming an ionic complex from the transition metal compound or its derivative, and an organic Al compound, and giving a stereospecific polyolefin having high mol. and narrow mol.wt. distribution.

CONSTITUTION: The catalyst giving polymers having high mol.wts. and narrow mol.wt. distributions comprises (A) a transition metal compound of the formula (M is the 3-10th group metal element or the lanthanoid metal element in the periodic table; X is a σ -bonding ligand, a chelating ligand, a Lewis base; a is an integer of 0-6; Y is a group containing O, S, Se, C, N, P, Si, Sn, etc.; b is an integer of 1-4; c is an integer of 0-4; A is a cross-linking group comprising an atomic group containing O, S, Se, C, N, P, Si, Sn, B, etc.; B is an atomic group containing O, S, Se, C, N, P, Si, Sn, B, etc.; d is an integer of 1-6), (B) a compound capable of forming an ionic complex from the component A or its derivative, and (C) an organic Al compound.



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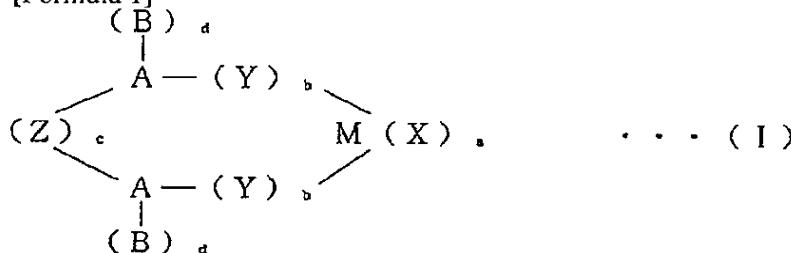
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CLAIMS

[Claim(s)]

[Claim 1] (A) General formula (I)

[Formula 1]



the inside of a formula, and M -- the metallic element of the 3-10th groups of a periodic table, or a lanthanoids sequence -- X shows a sigma-bond nature ligand, a chelate nature ligand, or a Lewis base, and a is the integer of 0-6. Y shows the basis containing O, S, Se, C, N, P, Si, and Sn, when X is plurality, even if X is the same each, it may differ, b is the integer of 1-4, and when Y is plurality, even if Y is the same each, it may differ Z shows the atomic group which contains O, S, Se, C, N, P, Si, Sn, and B with a bridge formation machine, c is the integer of 0-4, and when Z is plurality, even if Z is the same each, it may differ, A may show the atomic group which contains O, S, Se, C, N, P, Si, Sn, and B with a bridge formation machine, and even if A is the same each, it may differ B shows the atom or atomic group which consists of O, S, Se, C, N, P, Si, Sn, and B by the substituent which adjoins A. d is the integer of 1-6, and when B is plurality, even if B is the same each, it may differ The catalyst for olefin polymerizations characterized by containing the compound which can form an ionicity complex from the transition-metals compound expressed and the transition-metals compound of (B) ** (A) component, or its derivative.

[Claim 2] (A) The catalyst for olefin polymerizations characterized by containing the compound which can form an ionicity complex from the transition-metals compound shown by the general formula (I), the transition-metals compound of (B) ** (A) component, or its derivative, and the (C) organoaluminium compound.

[Claim 3] (B) The catalyst for olefin polymerizations according to claim 1 or 2 which is the ionicity compound with which the compound of a component reacts with the transition-metals compound of the (A) component, and forms an ionicity complex.

[Claim 4] (B) The catalyst for olefin polymerizations according to claim 1 or 2 whose compound of a component is aluminoxane.

[Claim 5] The manufacture method of the polyolefine characterized by carrying out copolymerization of homopolymerization or olefins, other olefins, and/or other monomers for olefins under existence of the catalyst for olefin polymerizations according to claim 1 to 4.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the manufacture method of a polyolefine using the new catalyst for olefin polymerizations, and this catalyst. If it says in more detail, this invention relates to the method of manufacturing efficiently the polyolefine which has the above-mentioned property using the catalyst for high activity soluble polymerizations which gives a stereoregularity polyolefine with narrow molecular weight distribution, and this catalyst for polymerizations in the amount of macromolecules.

[0002]

[Description of the Prior Art] Conventionally, as a high activity soluble olefin-curing catalyst, what consists of combination of a transition-metals compound and aluminoxane is known (JP,58-19309,A, JP,60-217209,A). moreover, ["a journal OBU JI American chemical society (J.Am.Chem.Soc.)" to which it is reported as active species of a soluble olefin-curing catalyst that an ionicity complex is useful -- the 81st volume, the 81st page (1959), the 82nd volume, the 1953rd page (1960), the 107th volume, and the 7219page(1985)] Moreover, it is an example which isolated this active species and was adapted for the olefin polymerization. "Journal OBU JI American chemical society (J.Am.Chem.Soc.)" JP,3-207704,A, the international patent public presentation No. 1723 [92 to], etc. can be mentioned as an example which used the organoaluminium compound together for the 108th volume, the 7410th page (1986), a ***** 1-No. 502636 official report, JP,3-139504,A, the Europe public presentation patent No. 468651, etc. to this active species further.

[0003] However, the polymer generated by the complex with the cyclopentadienyl system ligand used in such conventional technology had the trouble that the molecular weight of the polymer obtained was small, when reaction temperature performed a polymerization in an industrial process by efficient 70-200 degrees C or more than it. Moreover, according to the homogeneous-system catalyst, the method of obtaining a stereoregularity polyolefine is indicated variously (JP,61-130314,A, a JP,1-301704,A official report, JP,2-41303,A official report, etc.).

[0004] However, the obtained polymer has the problem that molecular weight is small, the top where a ligand with special substituents, such as an indenyl group, a substituent cyclopentadienyl group, or a fluorenyl group, is required for each catalyst for polymerizations used in these methods. Moreover, stereoregularity is not indicated although it is indicated by it that polypropylene is obtained even if there is no substitution cyclo pen dienyl machine in the international patent public presentation No. 2370 [87 to].

[0005]

[Problem(s) to be Solved by the Invention] this invention is the basis of such a situation and is made for the purpose of offering the method of manufacturing efficiently the polyolefine which has the above-mentioned property, using the new catalyst for high activity soluble polymerizations which gives a stereoregularity polyolefine with narrow molecular weight distribution in the amount of macromolecules, and this catalyst for polymerizations.

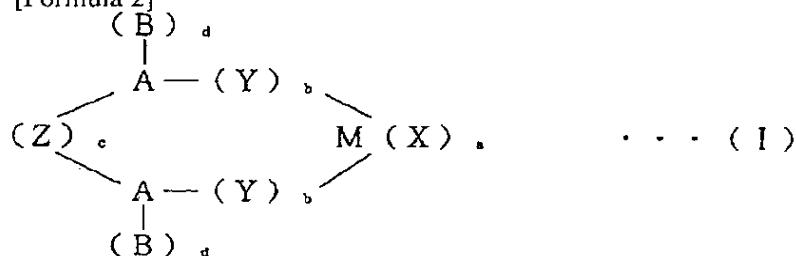
[0006]

[Means for Solving the Problem] This invention persons found out that the purpose could be attained according to the specific transition-metals compound, the compound which can form an ionicity complex from this transition-metals compound or its derivative, and the catalyst for polymerizations which contains an organoaluminium compound by the case, as a result of repeating research wholeheartedly, in order to attain the aforementioned purpose. this invention is completed based on this knowledge.

[0007] That is, this invention is the (A) general formula (I).

[0008]

[Formula 2]

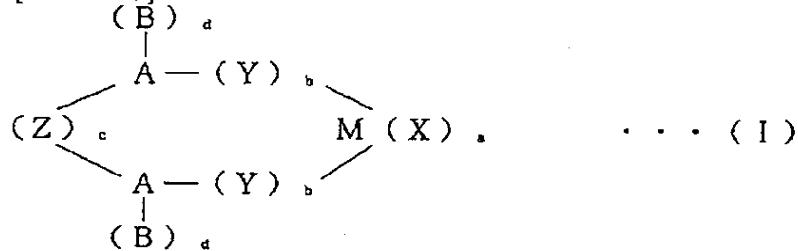


[0009] the inside of a formula, and M -- the metallic element of the 3-10th groups of a periodic table, or a lanthanoids sequence -- X shows a sigma-bond nature ligand, a chelate nature ligand, or a Lewis base, and a is the integer of 0-6. Y shows the basis containing O, S, Se, C, N, P, Si, and Sn, when X is plurality, even if X is the same each, it may differ, b is the integer of 1-4, and when Y is plurality, even if Y is the same each, it may differ Z shows the atomic group which contains O, S, Se, C, N, P, Si, Sn, and B with a bridge formation machine, c is the integer of 0-4, and when Z is plurality, even if Z is the same each, it may differ, A may show the atomic group which contains O, S, Se, C, N, P, Si, Sn, and B with a bridge formation machine, and even if A is the same each, it may differ B shows the atom or atomic group which consists of O, S, Se, C, N, P, Si, Sn, and B by the substituent which adjoins A. d is the integer of 1-6, and when B is plurality, even if B is the same each, it may differ The compound which can form an ionicity complex from the transition-metals compound expressed, the transition-metals compound of (B) ** (A) component, or its derivative, And the catalyst for olefin polymerizations characterized by containing the (C) organoaluminium compound by the case, And the manufacture method of the polyolefine characterized by carrying out copolymerization of homopolymerization or olefins, other olefins, and/or other monomers for olefins is offered under existence of this catalyst for olefin polymerizations.

[0010] In addition, the catalyst for polymerizations of this invention also includes the thing which made support support (A) or (B) at least among the above-mentioned things. It sets to the polymerization catalyst of this invention, and is a general formula (I) as a (A) component.

[0011]

[Formula 3]



[0012] It comes out and the transition-metals compound expressed is used. In the above-mentioned general formula (I), M shows the metallic element of the 3-10th groups of a periodic table, or a

lanthanoids sequence. X shows a sigma-bond nature ligand, a chelate nature ligand, or a Lewis base, a is the integer of 0-6, and when X is plurality, even if X is the same each, it may differ As an example of X, alkoxy groups, such as alkyl groups, such as the halogenide of a fluorine, chlorine, a bromine, and iodine, a methyl group, an ethyl group, n-propyl group, an isopropyl machine, n-butyl, and an isobutyl machine, a methoxy machine, an ethoxy basis, n-propoxy group, an isopropoxy group, an n-butoxy machine, and an iso-butoxy machine, etc. are mentioned. Y shows the basis containing O, S, Se, C, N, P, Si, and Sn, b is the integer of 1-4, and when Y is plurality, even if Y is the same each, it may differ As an example of Y Chalcogen atoms, such as **-O-, -S-, and -Se-, and -CH₂- -C(CH₃)₂-, -C () [C₂] Hydrocarbon groups, such as H₅ 2-, -NH-, -N () [CH₃] -, -N(C₂H₅)-, -N () [C₆] Nitrogen atom content machines, such as H₅-, -PH-, -P () [CH₃] -, -P(C₂H₅)-, -P () [C₆] Tin atom content machines, such as silicon atom content machines, such as the Lynn atom content machines, such as H₅-, -SiH₂-, -Si(CH₃)₂-, and -Si(C₂H₅)₂-, -SnH₂-, -Sn(CH₃)₂-, and -Sn(C₂H₅)₂-, etc. are mentioned. [0013] Z shows the atomic group which contains O, S, Se, C, N, P, Si, Sn, and B with a bridge formation machine, c is the integer of 0-4, and when Z is plurality, even if Z is the same each, it may differ As an example of Z Hydrocarbon groups, such as nitrogen, such as chalcogen atoms, such as **-O-, -S-, and -Se, -NH-, -PH-, -N(CH₃)-, and -P(CH₃)-, or the Lynn atom content machine, -CH₂-, and -C(CH₃)₂-, -SiH₂-, -Si () [CH₃] Boron atom content machines, such as tin atom content machines, such as silicon atom content machines, such as 2-, -SnH₂-, and -Sn(CH₃)₂-, -BH-, -B(CH₃)-, and -BF-, etc. are mentioned. A shows the atomic group which contains O, S, Se, C, N, P, Si, Sn, and B with a bridge formation machine, and A may be the same each and may differ. The chain-like hydrocarbon group of the carbon numbers 1-20, such as a ring-compound residue of the carbon numbers 1-20 which contain hetero atoms, such as a cyclic-hydrocarbon residue of the carbon numbers 1-20, such as benzene, naphthalene, and an anthracene, a pyridine, a quinoline, a thiophene, and a furan, as an example of A, -CH-, -CH₂-CH-, and -CH₂-CH₂-CH-, etc. is mentioned.

[0014] B shows the atom or atomic group which consists of O, S, Se, C, N, P, Si, Sn, and B by the substituent which adjoins A, d is the integer of 1-6, and when B is plurality, even if B is the same each, it may differ As an example of B **-Si (CH₃)₃, -Si () [C₂]H₅ 3 and -Si (C₆H₅)₃ etc. -- a silyl machine, -C(CH₃)₃, -C(C₂H₅)₃, and -C(C₃H₇)₃, -C(C₄H₉)₃, and -C(C₆H₅)₃ etc. -- it is the hydrocarbon group of carbon numbers 4-20

trimethylsilyl -2, 2'-phenoxy) zirconium dibenzyl, 1 and 1'-screw (3, 3'-trimethylsilyl -2, 2'-phenoxy) zirconium JIMETOKISHIDO, 1 and 1'-screw (3, 3'-trimethylsilyl -2, 2'-phenoxy) zirconium diisopropoxide, 1 and 1'-screw (3, 3'-triphenylmethyl -2, 2'-phenoxy) zirconium dichloride, A 1 and 1'-screw (3, 3'-triphenylmethyl -2, 2'-phenoxy) zirconium dimethyl, A 1 and 1'-screw (3, 3'-triphenylmethyl -2, 2'-phenoxy) zirconium dibenzyl, 1 and 1'-screw (3, 3'-triphenylmethyl -2, 2'-phenoxy) zirconium JIMETOKISHIDO, 1 and 1'-screw (3, 3'-triphenylmethyl -2, 2'-phenoxy) zirconium diisopropoxide, 1 and 1'-screw (3, 3'-t-butyl -2, 2'-phenoxy) zirconium dichloride, A 1 and 1'-screw (3, 3'-t-butyl -2, 2'-phenoxy) zirconium dimethyl, A 1 and 1'-screw (3, 3'-t-butyl -2, 2'-phenoxy) zirconium dibenzyl, 1 and 1'-screw (3, 3'-t-butyl -2, 2'-phenoxy) zirconium JIMETOKISHIDO, 1 and 1'-screw (3, 3'-t-butyl -2, 2'-phenoxy) zirconium diisopropoxide etc. can mention what replaced the zirconium in these compounds by titanium and the hafnium. For example, 1 and 1'-screw (3, 3'-triphenyl silyl -2, 2'-naphthoxy) titanium dichloride, A 1 and 1'-screw (3, 3'-triphenyl silyl -2, 2'-naphthoxy) titanium dimethyl, A 1 and 1'-screw (3, 3'-triphenyl silyl -2, 2'-naphthoxy) titanium diisopropoxide, 1 and 1'-screw (3, 3'-triphenyl silyl -2, 2'-naphthoxy) titanium dichloride, A 1 and 1'-screw (3, 3'-trimethylsilyl -2, 2'-naphthoxy) titanium dimethyl, A 1 and 1'-screw (3, 3'-trimethylsilyl -2, 2'-naphthoxy) titanium dibenzyl, Although there is - screw (3, 3'-trimethylsilyl -2, 2'-naphthoxy) CHITANIUMUJI methoxide, and 1 and 1'-screw (3, 3'-trimethylsilyl -2, 2'-naphthoxy) titanium diisopropoxide etc., of course, it is not limited to these. Moreover, you may be the similar compound of other groups or the metallic element of a lanthanoids sequence. One sort of these transition-metals compounds may be used, and they may be used combining two or more sorts.

[0016] In the catalyst for polymerizations of this invention, the compound which can form an ionicity complex from the aforementioned transition-metals compound or its derivative as a (B) component is used. The ionicity compound which reacts with the transition-metals compound of the ((B-1)A) component, and forms an ionicity complex as this (B) component, aluminoxane (B-2), and a Lewis acid (B-3) can be mentioned. (B-1) If it is the ionicity compound which reacts with the transition-metals compound of the aforementioned (A) component, and forms an ionicity complex as a component, although anything can be used, it is the following general formula (II). (III) ([L1-R1] k+) p q ([Z]-) ...

[II]

([L2] k+) p q ([Z]-) ... [II]

(However, L2 is M2, R2 R3 M3, R43C, or R5 M3.) the anion, i.e., [M1 A1 A2 ... , to which two or more bases combined un-configuring nature anion [Z1] - with the element -- An] - and here [[Z2]- and here] -- [Z1]- (here -- it is -- M1 -- the 5-15th group element of a periodic table -- the 13-15th group element of a periodic table is shown preferably) A1 -An A hydrogen atom, a halogen atom, the alkyl group of carbon numbers 1-20, the dialkylamino machine of carbon numbers 2-40, the alkoxy group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, the aryloxy group of carbon numbers 6-20, the alkyl aryl machine of carbon numbers 7-40, the arylated-alkyl machine of carbon numbers 7-40, the halogenation hydrocarbon group of carbon numbers 1-20, the acyloxy machine of carbon numbers 1-20, an organic metalloid machine, or the hetero atom content hydrocarbon group of carbon numbers A1 -An Two or more may form the ring inside. n shows the integer of [(valence of the central metal M1)+1] . [Z2]- the logarithm (pKa) of the inverse number of an acid dissociation constant -ten or less Broensted acid -- the conjugate base of the combination of independent or a Broensted acid, and a Lewis acid or the conjugate base generally defined as super-strong acid is shown Moreover, the Lewis base may configurate. Moreover, R1 A hydrogen atom, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, an alkyl aryl machine, or an arylated-alkyl machine is shown, and it is R2. And R3 It is a cyclopentadienyl group, a substituent cyclopentadienyl group, an indenyl group or a fluorenyl group, and R4, respectively. The alkyl group, the aryl group, alkyl aryl machine, or arylated-alkyl machine of carbon numbers 1-20 is shown. R5 Large annular ligands, such as a tetrapod phenyl porphyrin and a phthalocyanine, are shown. In the ionic valence of [L1-R1] and [L2], k is the integer of 1-3 and p is one or more integers and q= (kxp). M2 A periodic table 1-3rds, 11-13, and 17 group element are included, and it is M3. The 7-12th group element of a periodic table is shown.] It can come

out and what is expressed can be used suitably.

[0017] Here, it is L1. As an example Ammonia, a monomethylamine, an aniline, a dimethylamine, a diethylamine, N-methylaniline, a diphenylamine, N,N-dimethylaniline, a trimethylamine, a triethylamine, tree n butylamine, a methyl diphenylamine, a pyridine, p-BUROMO - N, Amines, such as N-dimethylaniline and p-nitroglycerine-N,N-dimethylaniline, Nitril, such as ester, such as thioether, such as phosphines, such as a triethyl phosphine, triphenyl phosphine, and diphenylphosphine, and tetrahydrothiophene, and an ethyl benzoate, an acetonitrile, and a benzonitrile, can be mentioned. R1 As an example, hydrogen, a methyl group, an ethyl group, a benzyl, a trityl radical, etc. can be mentioned, and it is R2 and R3. As an example, a cyclopentadienyl group, a methylcyclopentadienyl machine, an ethylcyclopentadienyl machine, a pentamethylcyclopentadienyl group, etc. can be mentioned. R4 As an example, a phenyl group, p-tolyl group, p-methoxyphenyl machine, etc. can be mentioned, and it is R5. A tetraphenylporphine, a phthalocyanine, an allyl compound, metallyl, etc. can be mentioned as an example. M2 [moreover,] as an example -- Li, Na, K, Ag, Cu, Br, I, and I3 etc. -- it can mention -- M3 Mn, Fe, Co, nickel, Zn, etc. can be mentioned as an example.

[0018] (Moreover, [Z1]-, i.e., [M1 A1 A2, ... It sets to An] and is M1. As an example, B and aluminum are preferably mentioned for B, aluminum, Si, P, As, Sb, etc.) Moreover, A1 and A2 -An As an example As a dialkylamino machine, a dimethylamino machine, a diethylamino machine, etc., As an alkoxy group or an aryloxy group, a methoxy machine, an ethoxy basis, an n-butoxy machine, a phenoxy machine, etc., As a hydrocarbon group, a methyl group, an ethyl group, n-propyl group, an isopropyl machine, n-butyl, an isobutyl machine, n-octyl machine, n-ray KOSHIRU machine, a phenyl group, p-tolyl group, a benzyl, a 4-t-butylphenyl group, 3, 5-dimethylphenyl machine, etc., As a halogen atom, as a fluorine, chlorine, a bromine, iodine, and a hetero atom content hydrocarbon group p-fluoro phenyl group, 3, a 5-difluoro phenyl group, a pentachlorophenyl group, 3 and 4, 5-trifluoro RUORO phenyl group, a pentafluorophenyl machine, 3, 5-screw (trifluoromethyl) phenyl group, a screw (trimethylsilyl) methyl group, etc., A pen reservoir chill antimony machine, a trimethylsilyl machine, a trimethyl gel mill machine, a diphenyl arsine machine, a dicyclohexyl antimony machine, diphenyl boron, etc. are mentioned as an organic metalloid machine.

[0019] moreover The anion of un-configurating nature, i.e., pKa, is the conjugate base of the combination of the Broensted-acid independent not more than -10 or a Broensted acid, and a Lewis acid [Z2]. - As an example ** trifluoromethane sulfonic-acid anion () [CF3] SO3-, screw (trifluoromethane sulfonyl) methyl anion, screw (trifluoromethane sulfonyl) benzyl anion, screw (trifluoromethane sulfonyl) amide, and perchloric acid anion (ClO4)-, a trifluoroacetic-acid anion () [CF3] CO2-, a hexafluoro antimony anion () [SbF6] -, a fluorosulfonic acid anion () [FSO3] -, a chlorosulfonic-acid anion () [ClSO3] -, a fluorosulfonic acid anion / 5-antimony fluoride (FSO3/SbF5) -, a fluorosulfonic acid anion / 5-fluoride arsenic (FSO3 / AsF5) -, a trifluoromethane sulfonic acid / 5-antimony fluoride () [CF3] SO3 / SbF5- etc. -- it can mention

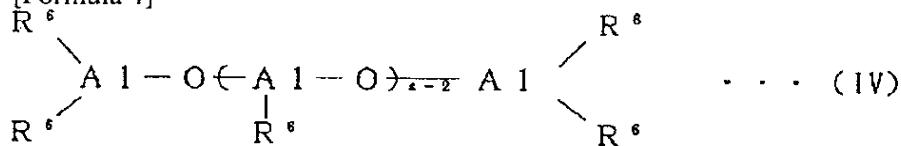
[0020] As an example of the ionicity compound which reacts with the transition-metals compound of such an aforementioned (A) component, and forms an ionicity complex, i.e., (B-1), a component compound Tetrapod phenyl triethyl-borate ammonium, tetrapod phenyl boric-acid tree n-butyl ammonium, tetrapod phenyl boric-acid trimethylammonium, a tetrapod phenyl boric-acid tetraethylammonium, tetrapod phenyl methyl-borate (tree n-butyl) ammonium, A tetrapod phenyl boric-acid benzyl Ammonium, tetrapod phenyl boric-acid dimethyl diphenyl ammonium, tetrapod phenyl boric-acid triphenyl (methyl) ammonium, tetrapod phenyl trimethyl-borate anilinium, tetrapod phenyl methyl-borate pyridinium, (Tree n-butyl) Tetrapod phenyl-boric-acid benzyl pyridinium, a tetrapod phenyl methyl borate (2-cyano pyridinium), Tetrakis Triethyl-borate ammonium, (Pentafluorophenyl) Tetrakis Boric-acid tree n-butyl ammonium, tetrakis (pentafluorophenyl) boric-acid triphenyl ammonium, tetrakis (pentafluorophenyl) boric-acid tetrapod-n-butyl ammonium, tetrakis (Pentafluorophenyl) A boric-acid tetraethylammonium, tetrakis (pentafluorophenyl) boric-acid benzyl (tree n-butyl) ammonium, tetrakis (pentafluorophenyl) methyl-borate diphenyl ammonium, tetrakis (Pentafluorophenyl) A boric-acid triphenyl (Pentafluorophenyl) Ammonium, tetrakis (Methyl) Methyl-borate anilinium, tetrakis (pentafluorophenyl) boric-acid dimethyl anilinium, tetrakis

(pentafluorophenyl) trimethyl-borate anilinium, tetrakis (pentafluorophenyl) methyl-borate pyridinium, (Pentafluorophenyl) Tetrakis (pentafluorophenyl) boric-acid benzyl pyridinium, a tetrakis (pentafluorophenyl) methyl borate (2-cyano pyridinium), A tetrakis (pentafluorophenyl) boric-acid benzyl (2-cyano pyridinium), A tetrakis (pentafluorophenyl) methyl borate (4-cyano pyridinium), Tetrakis Boric-acid triphenyl phosphonium, tetrakis [screw (3, 5-difluoromethyl) phenyl] boric-acid dimethyl anilinium, tetrapod phenyl boric-acid ferro SENIUMU, tetrapod phenyl boric-acid silver, tetrapod phenyl boric-acid trityl, (Pentafluorophenyl) Tetrapod phenyl boric-acid tetrapod phenyl porphyrin manganese, tetrakis (pentafluorophenyl) boric-acid ferro SENIUMU, a tetrakis (pentafluorophenyl) boric acid (1 and 1'-dimethyl ferro SENIUMU), Tetrakis (pentafluorophenyl) boric-acid decamethyl ferro SENIUMU, tetrakis (pentafluorophenyl) boric-acid silver, Tetrakis Boric-acid trityl, tetrakis (Pentafluorophenyl) A boric-acid lithium, tetrakis (Pentafluorophenyl) A sodium borate, tetrakis (Pentafluorophenyl) (Pentafluorophenyl) Boric-acid TEORA phenyl porphyrin manganese, tetrafluoroboric silver, a hexafluoro silver phosphate, hexafluoro arsenic ***, perchloric acid silver, trifluoroacetic-acid silver, trifluoromethane sulfonic-acid silver, etc. can be mentioned.

[0021] One sort of ionicity compounds which are this (B-1) component and which react with the transition-metals compound of a ** (A) component, and form an ionicity complex may be used, and may be used combining two or more sorts. On the other hand, as aluminoxane of a component (B-2), it is a general formula (IV).

[0022]

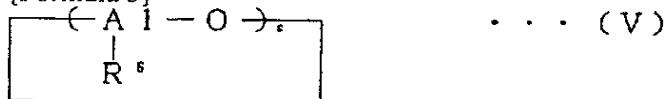
[Formula 4]



[0023] -- the inside of a formula, and R6 -- carbon numbers 1-20 -- desirable -- hydrocarbon groups, such as an alkyl group of 1-12, an ARUKENIRU machine, an aryl group, and an arylated-alkyl machine, and s -- polymerization degree -- being shown -- usually -- 3-50 -- it is the integer of 7-40 preferably -- the chain-like aluminoxane shown by), and a general formula (V)

[0024]

[Formula 5]



[0025] -- R6 and s are the same as the above among a formula The annular aluminoxane shown by) can be mentioned. What is necessary is for there to be especially no limitation about the means, and just to make it react according to a well-known method, although the method of contacting alkylaluminum and condensing agents, such as water, is mentioned as a manufacturing method of the aforementioned aluminoxane. For example, there is a method to which dissolve ** organoaluminium compound in the organic solvent, add the organoaluminium compound at the beginning at the time of the method of contacting this in water, and ** polymerization, make a trialkylaluminium react to the method and ** tetrapod ARUKIRUJI aluminoxane to which the water of crystallization contained in the method of adding water behind, ** metal salt, etc. and the water of adsorption to an inorganic substance or the organic substance are made to react with an organoaluminium compound, and water is made to react further. In addition, as aluminoxane, you may be the thing of toluene insolubility. One sort of these aluminoxane may be used and it may be used combining two or more sorts.

(B-3) There may not be especially a limit about the Lewis acid of a component, and an organic compound or a solid-state-like inorganic compound is sufficient. A boron compound, an aluminium compound, etc. are used as an organic compound, and a magnesium compound, an aluminium

compound, etc. are preferably used as an inorganic compound. As this aluminium compound, for example, a screw (2, 6-G t-butyl-4-methylphenoxy) aluminum methyl, an aluminum (1 and 1-BI-2-naphthoxy) methyl, etc. As a magnesium compound, for example, a magnesium chloride, diethoxy magnesium, etc. As an aluminium compound, an aluminium oxide, an aluminium chloride, etc. As a boron compound **, for example, triphenyl boron, tris Boron, tris [3, 5-screw (Pentafluorophenyl) Phenyl] boron and tris [(Trifluoromethyl) Phenyl] boron, trimethyl boron, a boron triethyl, tree n-butyl boron, tris (fluoro methyl) boron, tris (pentafluoro ethyl) boron, tris (nona fluoro butyl) boron, tris (2, 4, 6-truffe RUORO phenyl) boron, (4-fluoro methyl) Tris Boron, tris [3, 5-screw (3, 5-difluoro) Phenyl] boron, a screw (Trifluoromethyl) Fluoro boron, diphenyl fluoro boron, screw (pentafluorophenyl) chloro boron, dimethyl fluoro boron, diethyl fluoro boron, di-n-butyl fluoro boron, pentafluorophenyl difluoro boron, phenyl difluoro boron, (Pentafluorophenyl) Pentafluorophenyl dichloro boron, methyl difluoro boron, ethyl difluoro boron, n-butyl difluoro boron, etc. are mentioned. One sort of these Lewis acids may be used, and they may be used combining two or more sorts.

[0026] the case where a compound is used for the operating rate of (A) catalyst component and (B) catalyst component in the catalyst for polymerizations of this invention as a (B) catalyst component (B-1) -- a mole ratio -- desirable -- 10:1-1:100, and the case where the range of 2:1-1:10 was desirable, and (B-2) uses a compound more preferably -- a mole ratio -- desirable -- 1:1-1:1000000 -- the range of 1:10-1:10000 is more preferably desirable the operating rate of the catalyst component (aforementioned [A]) and a catalyst (B-3) component -- a mole ratio -- it is -- desirable -- 1:0.1-1:2000 -- more -- desirable -- 1:0.2-1:1000 -- the range of 1:0.5-1:500 is still more preferably desirable moreover, independent [in (B-1), (B-2), etc.] (B-3) as a catalyst component (B) -- or two or more sorts can be combined and it can also use The catalyst for polymerizations of this invention may contain the aforementioned (A) component and the (B) component as a principal component, and may contain the (A) component, the (B) component, and the (C) organoaluminium compound as a principal component. Here, as an organoaluminium compound of the (C) component, it is general formula (VI) R₇ r AlQ_{3-r}. ... The compound shown by (VI) and (R7 showing the alkyl group of carbon numbers 1-10 among a formula, Q showing a hydrogen atom, the alkoxy group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, or a halogen atom, and r being the integer of 1-3) is used.

[0027] The aforementioned general formula (VI) As an example of the compound shown, a trimethylaluminum, a triethylaluminum, triisopropyl aluminum, triisobutylaluminum, dimethyl aluminum chloride, a diethylaluminum chloride, methyl aluminum dichloride, ethyl aluminum dichloride, a dimethyl aluminum fluoride, a diisobutyl aluminum hydride, a diethyl aluminum hydride, ethylaluminum sesquichloride, etc. are mentioned. One sort of these organoaluminium compounds may be used and they may be used combining two or more sorts. the operating rate of the catalyst component (aforementioned [A]) and (C) catalyst component -- a mole ratio -- desirable -- 1:1-1:10000 -- more -- desirable -- 1:5-1:2000 -- the range of 1:10 or 1:1000 is still more preferably desirable Although the polymerization activity per transition metals can be raised by using (** C) catalyst component, if many [not much], while an organoaluminium compound will become useless, it remains so much in a polymer and is not desirable.

[0028] In this invention, even if there are few catalyst components, a kind can be supported and used for suitable support. Although there is especially no limit about the kind of this support and both inorganic-oxide support the other inorganic support and organic support can be used, inorganic-oxide support or the other inorganic support is especially desirable. Specifically as inorganic-oxide support, it is SiO₂, aluminum 2O₃, MgO, ZrO₂, TiO₂, Fe 2O₃, B-2 O₃, and CaO, ZnO, BaO and ThO₂. Such mixture, for example, a silica alumina, a zeolite, a ferrite, glass fiber, etc. are mentioned. Especially in these, they are SiO₂ and aluminum 2O₃. It is desirable. In addition, the above-mentioned inorganic-oxide support may contain a small amount of carbonate, a nitrate, a sulfate, etc. on the other hand -- as support other than the above -- MgCl₂ and Mg (OC two H₅)₂ etc. -- general formula MgR₈ X_{1-y} represented with a magnesium compound etc. The magnesium compound expressed, its complex salt, etc. can be mentioned. Here, it is R₈. The alkyl group of carbon numbers 1-20, the alkoxy group of carbon numbers 1-20 or the aryl group of carbon numbers 6-20, and X₁ The alkyl group of a halogen atom or carbon

numbers 1-20 is shown, and 0-2y of x are ** and x+y=2 in 0-2, every -- R8 and every -- XI respectively -- being the same -- moreover, even if it differs, you may be

[0029] Moreover, as organic support, polymers, such as polystyrene, polyethylene, polypropylene, substitution polystyrene, and a polyarylate, starch, carbon, etc. can be mentioned. as the support used in this invention -- MgCl₂, MgCl (OC two H₅), Mg (OC two H₅)₂, SiO₂, and aluminum 2O₃ etc. -- it is desirable. Moreover, although the character of support changes with the kinds and processes, 10-200 micrometers of mean particle diameters are 1-300 micrometers usually 20-100 micrometers more preferably. If particle size is small, the fines in a polymer will increase, and if particle size is large, the big and rough particle in a polymer will increase, and it will become the fall of bulk density, and the cause of plugging of a hopper. moreover, the specific surface area of support -- usually -- 1-1000m² / g - desirable -- 50-500m² / g, and pore volume -- usually -- 0.1-5cm³ / g -- they are 0.3-3cm³ / g preferably When either specific surface area or pore volume deviates from the above-mentioned range, catalytic activity may fall. In addition, it can ask for specific surface area and pore volume from the volume of the nitrogen gas adsorbed according to the BET adsorption method (refer to journal OBU JI American chemical SOSAIETI, the 60th volume, and the 309th page (1983)). Furthermore, as for the above-mentioned support, it is usually desirable to calcinate and use at 200-800 degrees C preferably 150-1000 degrees C.

[0030] When [of a catalyst component] making the aforementioned support support a kind at least, it is desirable to make both (A) catalyst component and (B) catalyst component support preferably either [at least] (A) catalyst component or (B) catalyst component. About the method of making this support supporting either [at least] the (A) component or the (B) component How to mix at least one side and support of ** (A) component and the (B) component, for example, although not restricted especially, ** After processing support with an organoaluminium compound or a halogen content silicon compound, How to mix with either [at least] the (A) component or the (B) component in an inert solvent, ** The method to which support, the (A) component and/or the (B) component, an organoaluminium compound, or a halogen content silicon compound is made to react, ** Face the catalytic reaction of the method of mixing with the (B) component or the (A) component, the method of mixing the catalytic-reaction object of ** (A) component and the (B) component with support, ** (A) component, and the (B) component after making support support the (A) component or the (B) component. The method of making support living together etc. can be used. In addition, the organoaluminium compound of the (C) component can also be added in the reaction of the above-mentioned **, **; and **.

[0031] Thus, after the acquired catalyst once performs solvent distilling off and takes it out as a solid-state, it may be used for a polymerization, and you may use it for a polymerization as it is. Moreover, a catalyst can be made to generate in this invention by performing support operation to one [at least] support of the (A) component and the (B) component within a polymerization system. For example, the organoaluminium compound of the aforementioned (C) component is further added as occasion demands with either [at least] the (A) component or the (B) component and support, and they are olefins, such as ethylene, Ordinary-pressure - 20 kg/cm² In addition, the method of performing precuring at -20-200 degrees C for 1 minute to about 2 hours, and making a catalyst particle generating can be used.

[0032] In this invention the operating rate of the aforementioned compound (B-1) component and support It is preferably desirable 1:5-1:10000, and to be more preferably referred to as 1:10-1:500. the operating rate of a component (B-2) and support It is preferably desirable 1:0.5-1:1000 and to be more preferably referred to as 1:1-1:50 at a weight ratio, and, as for the operating rate of a component (B-3) and support, it is preferably desirable 1:5-1:10000, and to be more preferably referred to as 1:10-1:500 at a weight ratio. When mixing and using two or more sorts as a catalyst component (B), it is desirable for the operating rate of a ** (B) component and support to be in above-mentioned within the limits by the weight ratio. Moreover, the operating rate of the (A) component and support is a weight ratio, and it is preferably desirable 1:5-1:10000, and to be more preferably referred to as 1:10-1:500. When the operating rate of a ** (B) component [(B-1)a component, a component (B-2), or (B-3) a component] and support or the operating rate of the (A) component and support deviates from the above-mentioned

range, activity may fall. thus, the mean particle diameter of the catalyst for polymerizations of the prepared this invention -- usually -- 2-200 micrometers -- desirable -- 10-150 micrometers -- especially - - desirable -- 20-100 micrometers -- it is -- specific surface area -- usually -- 20-1000m² / g -- they are 50-500m² / g preferably When a mean particle diameter is less than 2 micrometers, the fines in a polymer may increase, and when it exceeds 200 micrometers, the big and rough particle in a polymer may increase. When specific surface area is under 20m² / g, activity may fall, and when 1000m² / g is exceeded, the bulk density of a polymer may fall. Moreover, in the catalyst of this invention, it is usually desirable [especially the amount of transition metals in 100g of support] that they are 0.1-2g 0.05-10g. the amount of transition metals -- the above -- when out of range, activity is low and there is a bird clapper Thus, advantageous high bulk density and the polymer which has the outstanding particle size distribution can be industrially obtained by supporting to support.

[0033] According to the manufacture method of the polyolefine of this invention, homopolymerization of olefins or olefins and other olefins, and/or copolymerization (copolymerization between [which it is got blocked and is different species] olefins, copolymerization with olefins and other monomers, or copolymerization with both olefins of a different kind and other monomers) with other monomers can be suitably performed using the catalyst for polymerizations mentioned above. Although there is especially no limit about these olefins, the alpha olefin of carbon numbers 2-20 is desirable. As this alpha olefin, ethylene, a propylene, 1-butene, a 3-methyl-1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecen, 1-tetrapod decene, 1-hexa decene, 1-octadecene, 1-ray KOSEN, etc. can be mentioned. Moreover, what is necessary is just to select suitably from the above-mentioned olefins about other olefins mentioned above.

[0034] In this invention, one sort of above-mentioned olefins may be used, and it may be used combining two or more sorts. When performing copolymerization of two or more sorts of olefins, the above-mentioned olefins can be combined arbitrarily. the case where the operating rate in that case carries out copolymerization of a propylene, ethylene or ethylene, and the alpha olefin of carbon numbers 3-10 -- the copolymerization ratio (mole ratio) of a propylene, ethylene or ethylene, and the alpha olefin of carbon numbers 3-10 -- usually -- 99.9:0.1 to 0.1:99.9 -- it is preferably chosen in 99.5:0.5 to 75.0:25.0 moreover, as other monomers which may be made to carry out copolymerization of the above-mentioned olefins and other monomers, and are used in this invention in this case For example, vinyl aromatic compounds, such as styrene, p-methyl styrene, isopropyl styrene, and t-butyl styrene, butadiene; -- isoprene; -- chain-like diolefins, such as 1 and 5-hexadiene, -- Norbornene; 1, 4, 5, 8-dimethano - Annular olefins, such as 1, 2, 3, 4,a [4], 5, 8, and 8a-octahydronaphthalene;2-norbornene Annular diolefins, such as norbornadiene, 5-ethylidene norbornene, 5-vinyl norbornene, and a dicyclopentadiene Lactone, such as unsaturation ester, such as an ethyl acrylate and a methyl methacrylate, a beta propiolactone, beta-butyrolactone, and gamma-butyrolactone Lactams, such as an epsilon caprolactam and delta-valerolactam, an epoxy propane; epoxide, such as 1 and 2-epoxy butane, can be mentioned. In addition, the polymerization catalyst of this invention is not only used for the polymerization of the aforementioned olefins, but it can use it for polymerizations other than olefins.

[0035] In this invention, although especially a polymerization method is not restricted but which methods, such as a slurry polymerization method, a vapor-phase-polymerization method, a bulk-polymerization method, a solution polymerization method, and a suspension-polymerization method, may be used, a slurry polymerization method and especially a vapor-phase-polymerization method are desirable. About polymerization conditions, -50-200 degrees C of polymerization temperature are -100-250 degrees C usually 0-130 degrees C more preferably. Moreover, for the operating rate of the catalyst over a reaction raw material, a raw material monomer / the above-mentioned (A) component (mole ratio) is 1-108, especially 100-105 preferably. A bird clapper is desirable. furthermore, polymerization time -- usually -- 5 minutes - 10 hours and reaction pressure -- desirable -- ordinary-pressure - 200 kg/cm² G -- it is ordinary-pressure - 100 kg/cm² G especially preferably As the regulation method of the molecular weight of a polymer, selection of the kind of each catalyst component, the amount used, and polymerization temperature and a further have a polymerization under hydrogen existence etc. When using a polymerization solvent, halogenated hydrocarbons, such as aliphatic hydrocarbon, such as

alicyclic hydrocarbon, such as aromatic hydrocarbons, such as benzene, toluene, a xylene, and ethylbenzene, a cyclopentane, a cyclohexane, and a methylcyclohexane, a pentane, a hexane, a heptane, and an octane, chloroform, and a dichloromethane, etc. can be used. These solvents may use a kind independently and may combine two or more sorts of things. Moreover, you may use monomers, such as an alpha olefin, as a solvent. In addition, a non-solvent can perform depending on a polymerization method. Thus, although especially the molecular weight of the polymer obtained is not restricted, g of limiting viscosity [eta] (it measures in 135-degree-C decalin) is desirable in 0.1 deciliters /or more, and itsg is especially desirable in 0.2 deciliters /or more.

[0036] In this invention, precuring can be performed using the aforementioned catalyst for polymerizations. Although precuring can be performed by contacting a little olefin for a solid-state catalyst component, there is especially no limit in the method, and a well-known method can be used. Although what especially a limit does not have and was illustrated above about the olefin used for precuring, the same thing, for example, ethylene, the alpha olefins of carbon numbers 3-20, or such mixture can be mentioned, it is advantageous to use the same olefin as the olefin used in this polymerization. Moreover, -10-130 degrees C of precuring temperature are -20-200 degrees C usually 0-80 degrees C more preferably. In precuring, inert hydrocarbon, aliphatic hydrocarbon, an aromatic hydrocarbon, a monomer, etc. can be used as a solvent. Especially a desirable thing is aliphatic hydrocarbon in these. Moreover, a non-solvent may perform precuring. Especially in precuring, it is desirable to prepare conditions so that 1-10000g of amounts of the precuring product to which 0.2 deciliters /or more of limiting viscosity of a precuring product [eta] (it measures in 135-degree-C decalin) receive per 1mm mol of transition-metals components in 0.5 deciliters [g] /or more and a catalystg may be set especially to 10-1000g.

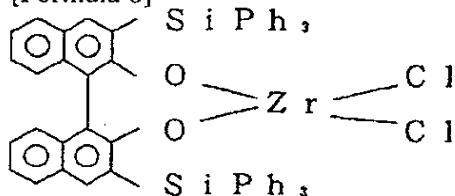
[0037]

[Example] Next, although an example and the example of comparison explain this invention to a detail further, this invention is not limited at all by these examples.

Example 1 The nitrogen purge of the 1l. autoclave in which isotactic polypropylene (IPP) carried out manufacture heating reduced pressure drying was carried out, and under room temperature nitrogen, 400ml of toluene and the 1mm mol of triisobutylaluminum were put in, and it stirred for 10 minutes. Subsequently, 1 and 1'-screw (3, 3'-triphenyl silyl -2, 2'-naphthoxy) zirconium dichloride dissolved in toluene under nitrogen. 10micromol -- the 10micro ([Me₂ PhNH] and [B(C₆ F₅)₄]) (Me shows methyl group and Ph shows phenyl group here) mol of boron compounds after putting in and stirring for 5 minutes was put in, and it stirred for 5 minutes again. The polymerization was carried out for 1 hour, introducing 3 atmospheric pressure of propylenes continuously keeping a solution at 20 degrees C. IPP0.32g was obtained by drying with a methanol the white solid-state which added a methanol/solution of hydrochloric acid to after [a reaction end] **, *****, and the reactant, and was obtained under reduced pressure after several times washing. When the melting point of this thing was measured, it was 140 degrees C. In addition, 1 and 1'-screw (3, 3'-triphenyl silyl -2, 2'-naphthoxy) zirconium dichloride has the structure shown below.

[0038]

[Formula 6]



[0039] Example 2 In the manufacture example of polyethylene (PE), PE6.2g was obtained by carrying out a polymerization like an example 1 except having changed the propylene into ethylene and having made ethylene ** 8 atmospheric pressure and polymerization temperature into 80 degrees C. The

melting point of this thing was 137 degrees C.

[0040] example 3 a line -- to the 11. autoclave of manufactures of a low density polyethylene (LLDPE), at the room temperature, 360ml of toluene, 40ml of 1-octenes, and the 1mm mol of triisobutylaluminum were put in, and it stirred for 10 minutes 5micro mol of 1 and 1'- screw (3, 3'-triphenyl silyl -2, 2'-naphthoxy) zirconium dichloride was put in, and for 5 minutes, after stirring, the 5micro ([Me₂ PhNH] and [B(C₆F₅)₄]) mol of boron compounds was put in, and it stirred for 5 minutes again. Subsequently, the polymerization was carried out at 80 degrees C for 1 hour, having carried out the temperature up of the solution to 80 degrees C under nitrogen and in 5 minutes, and introducing 8 atmospheric pressure of ethylene continuously. LLDPE6.4g was obtained by performing the same after treatment as an example 1. The melting point of this thing was 123 degrees C.

[0041] Except having used examples 4-61 and 1'-screw (3, 3'-triphenyl silyl -2, 2'-naphthoxy) titanium dichloride, the polymerization was performed according to examples 1-3, and IPP, PE, and LLDPE were obtained. These yield and melting points are shown in the 1st table.

[0042]

[Table 1]

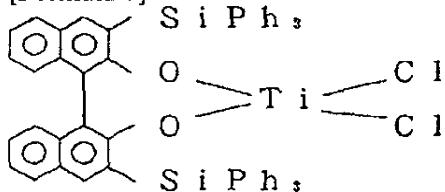
第 1 表

	ポリオレフィン 種類	收量 (g)	融点 (°C)
実施例 4	I P P	0. 2 0	1 3 9
実施例 5	P E	5. 9	1 3 9
実施例 6	L L D P E	1. 6	1 2 5

[0043] In addition, 1 and 1'-screw (3, 3'-triphenyl silyl -2, 2'-naphthoxy) titanium dichloride has the structure shown below.

[0044]

[Formula 7]

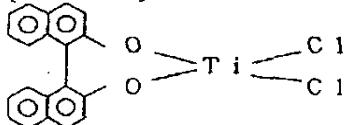


[0045] IPP0.30g was obtained by using an example 71 and 1'-screw (3, 3'-triphenyl silyl -2, 2'-naphthoxy) zirconium dichloride for a main catalyst, and using methyl aluminoxane as a co-catalyst, so that the metal atomic ratio to this main catalyst may be set to 1,000, and performing the polymerization of a propylene like an example 1. The melting point of this thing was 141 degrees C.

[0046] When the example 11 of comparison and 1'-screw (2 and 2'-naphthoxy) titanium dichloride were used for the main catalyst, and methyl aluminoxane was used as a co-catalyst so that the metal atomic ratio to this main catalyst might be set to 1,000, and the polymerization of a propylene was performed like the example 1, the yield of the obtained polymer is 0.15g and the melting point did not exist. In addition, 1 and 1'-screw (2 and 2'-naphthoxy) titanium dichloride has the structure shown below.

[0047]

[Formula 8]



[0048]

[Effect of the Invention] The catalyst for olefin system polymerizations of this invention is a high activity soluble catalyst, and a stereoregularity polyolefine with narrow molecular weight distribution is efficiently obtained in the amount of macromolecules by using this catalyst.

[Translation done.]